TRANSFORMATION OF AGROINDUSTRY EFFLUENTS WITH PESTICIDES CONTENT BY HETEROGENEOUS CATALYSIS

TRANSFORMACIÓN DE EFLUENTES AGROINDUSTRIALES CON CONTENIDO DE PESTICIDAS MEDIANTE CATÁLISIS HETEROGÉNEA

Inclined flat plate photo reactor for the treatment of agroindustry effluents with pesticides content

Luz Edith Barba-Ho, M.Sc.
Titular Professor
Environment and Natural Resources School
Universidad del Valle
Cali - Colombia.
luebarba@univalle.edu.co

Dorance Becerra, Ing.
Auxiliar Professor
Engineering and Management Faculty
Universidad Nacional de Colombia
Palmira - Colombia.
dbecerram@unal.edu.co

Viviana Angulo, Ing.
Sanitary Engineering
Environment and Natural Resources School .
Universidad del Valle
Cali - Colombia.
vivianaanguloingsanitaria@yahoo.es

**Recibido: 20 Octubre 2011 *Aceptado 1 Noviembre 2011*

Liliana Salazar, Ing.
Sanitary Engineering
Environment and Natural Resources School
Universidad del Valle
Cali - Colombia.
limasari1@hotmail.com.

RESUMEN

Un tratamiento fotocatalítico se utiliza para degradar contaminantes de las aguas residuales de alta generados durante las operaciones de lavado de tractores utilizados para la fumigación agroindustrial. Los efluentes contaminados con plaguicidas agroindustria Diuron, 2,4 D y Amethrine fue degradado usando un reactor de placa plana con dióxido de titanio (TiO2) como catalizador en suspensión y la radiación solar. Después del tratamiento fotocatalítico, la demanda química de oxígeno (DQO), carbono orgánico disuelto (COD) y la concentración de los pesticidas se midieron los parámetros de control del proceso de degradación de irradiaciones acumulado de 0, 18.75, 37.50, 56.25 y 75.00 1 kj.L. Los resultados experimentales mostraron una DQO 57% y el 23,9% de reducción de DOC para una energía máxima acumulada de 75 kj.L-1. La relación DQO / DOC resultó ser inversamente proporcional a la energía acumulada, lo que indica la transformación de los plaguicidas para los componentes con una estructura más simple molecular y por lo tanto, menos tóxicos y más fáciles de degradar a través de un post-tratamiento biológico junto con el proceso fotocatalítico.

PALABRAS CLAVE

Pesticidas, fotocatálisis, aguas residuales agroindustriales.

ABSTRACT

A photocatalytic treatment was used to degrade high pollutant wastewater generated during washing operations of tractors used for the agroindustrial fumigation. The contaminated agroindustry effluents with pesticides Diuron, 2,4D and Amethrine was degraded using a flat plate reactor with titanium dioxide (TiO_2) in suspension as catalyst and solar radiation. After photocatalytic treatment, the chemical oxygen demand (COD), dissolved organic carbon (DOC) and pesticides concentration were measured as control parameters of the degradation process for accumulated irradiations of 0, 18.75, 37.50, 56.25 and 75.00 kj.L^{-1}. The experimental results showed a 57% COD and 23.9% DOC reduction for a maximum accumulated energy of 75 kj.L^{-1}. The COD/DOC ratio was found to be inversely proportional to the accumulated energy, which indicates the transformation of pesticides to components with a simpler molecular structure and hence less toxic and easier to degrade through a biological post-treatment coupled to the photocatalytic process.

KEYWORDS

Pesticides, photocatalysis, agroindustry wastewaters.

1. INTRODUCTION

During last years, chemistry has developed several types of pesticides to protect crops and harvests from pest but taking care of the negative effect over human health. Their usefulness has been tested through the control of tropical sicknesses dispersed by insects (malaria, hemorrhagic dengue , paludism, etc) as well as a better efficiency per hectare of several crops resulting in socio-economical benefits (Gutierrez et al., 2004). Unfortunately, due to their high toxic and pollutant characteristics, an inappropriate treatment would result in negative environmental impacts and also a contrary economic effect in the harvest profitability.

Colombia is not far from this issue, as its geographic position provides particular climatic and biodiversity conditions that bring along numerous plagues attacks to the crops, requiring the application of several pesticides (Ministerio de Agricultura y Desarrollo Rural, 2006). The sugar cane is an important sector of the national economy in Colombia dealing with more than 200.000 hectares seeded with sugar cane which requires an extensive use of pesticides for pest control, brushes and occasionally to speed up its maturation process.

Pesticides most widely used are Diuron, 2,4 D and Amethrine. (Capurro, 2007), which are known to be highly toxic, persistent in soil and in superficial and underground waters generating high morbidity to living beings and also having a negative impact on the environment. At the same time, it has been shown that the degradation products of pesticides exhibit even a higher toxicity and are more persistent that the original substances from which they proceed. These compounds have a high toxicity potential and can contaminate all the spheres of the environment (Sorensen et al., 2003).

In order to decrease their effects, several biotechnological, chemical and physical technologies have been studied to treat wastewater containing pesticides. However, most of these technologies cannot be applied due to the high cost, low efficiency or they are not adequate for these residues. Nevertheless, new technologies have been developed that allow a total destruction or a toxic compounds modification from the chemical structure, so that they can be biodegradable and available to biological systems for final treatment. One of such technologies is the photo catalysis, which is being extensively applied in

Europe and North America with important results (Malato et al., 2001; Chu et al., 2004; Malato et al., 2002).

The photocatalysis is an advanced oxidation process (AOP's) that is characterized by the generation of highly oxidant species, mainly hydroxide radicals, effective for the oxidation and mineralization of several contaminants, such as pesticides, multi component organic mixtures and pharmaceutical wastes. This process has several comparative advantages, e.g. the use of solar energy, a fast reaction rate and the utilization of non hazardous reagents. Solar energy is an abundant resource and usable in a large area of the planet, especially in tropical zones like Colombia, and nonhazardous reagents are a positive issue because it minimizes the generation of residues to the environment.

2. EXPERIMENTAL

It was used a high concentrated mixture of wastewater from the sugar mill industry containing three type of pesticides, so the sample could be considered as extremely toxic and difficult to treat.

The wastewater was prepared with 2.5 Kg of Diuron (Karmex WG), 1.5 L of 2,4 D (2,4 D Amine 720), 3.0 L of Amethrine (Igram), 0.15 L de Inex-A (Cosmoagro) and 0.1 kg of Cosmoaguas (Cosmoagro) per each 150 L of preparation.

The assessed wastewater was prepared by adding 36 mL of pesticides mixture with a COD around 43,348 mg O_2 L^{-1} and 12 g of TiO_2 (600 mg $TiO_2.l^{-1}$). This amount of TiO_2 required in the flat plate reactor for this essay was previously optimized by the Research Group GAOX, Biosolar-Detox Project (10). The volume was completed to 20 L with tap water and the pH was adjusted to 6 units.

The treatment was carried out by heterogeneous photo catalysis with sunlight as radiation source in an acrylic inclined flat plate photo reactor and titanium dioxide - TiO_2 Degussa P25 as a catalyst, which was suspended in water. The photo reactor comprises an acrylic plate of 1.5 m long, 1 m wide and 0.1 m depth; the edges are stuck together with silicon, the liquid suspension flows over the plate which is fixed with PVC tubing and fittings supported on a metallic structure. The effective area of the plate is 1.5 m^2. A PVC tube with small perforations placed on top of the plate was used to distribute uniformly the suspension as a descendent film on the acrylic plate. The lower part of the plate has a collector that discharges the water, catalyst and suspension in the recycling tank with mixing by means of a pump. (Figure 1) shows a schematic representation of the photo reactor.

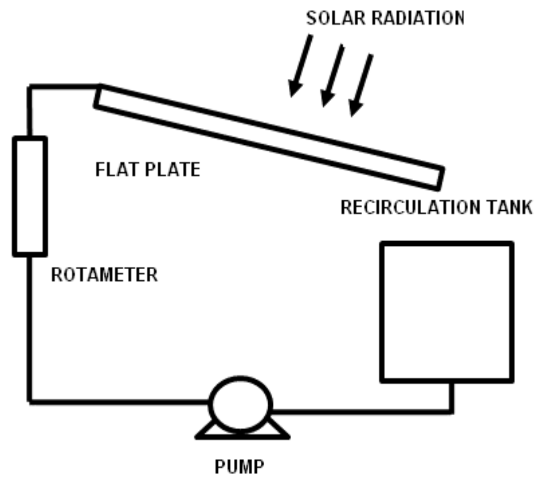


Figure 1. Inclined flat plate photo reactor

The recycling system comprises a pump with a constant flow 50 $l.min^{-1}$ with an electric monophasic engine AC 3/4" HP (3450 RPM, 115 V, 50/60 Hz and 1.3 Ampere). The flow was adjusted to 42 $l.min^{-1}$ through a 11/2" globe valve.

In order to follow the process, the time for sampling was determined as that corresponding to accumulated energies of 0, 18.75, 37.50, 56.25 y 75.00 $kj.L^{-1}$ during the operation time. The accumulated energy was calculated as follows:

$$Q_n = Q_{n-1} + \Delta t_n . I_n . A_f . V_T^{-1}$$

Where:

?t_n= Irradiation time = t_n-t_{n-1}

I_n = Average irradiation time, taken with a radiometer Acadus S50 sensitive in all the UV range, covering UVA and UVB

A_r = Reactor irradiated surface (1,5 m^2)

V_t = Treated total volume (20 L).

The sampling procedure (500 ml of solution per sample) was carried out directly in the feed tank in amber bottles to avoid photo degradation during the transport to the lab. The samples were filtrated with a membrane filter of 0.45 ?m pore size and then control parameters were measured, such as dissolved organic carbon (DOC) with a Shimadzu analyzer TOC-V CPH, chemical oxygen demand (COD) and pesticides concentration with a high resolution liquid chromatography (HPLC) analyzer according to the analytical techniques established in the Standard Methods for the Examination of Water and Wastewater / APHA, AWWA, WPFC (11). Also, pH and temperature were constantly monitored during the operation time.

In addition, control tests were carried out in order to determine possible loss of pesticides through a different mechanism from photo degradation, such as volatilization, adsorption on the surface of the catalysts or in the reactor walls and also due to rupture of chemical bonds by the radiant energy. The experiments consisted on: I) experiments with samples exposed to sunlight without TiO_2, and II) experiments in the darkness in the presence of TiO_2.

The treatment in the flat plate reactor was carried out up to reaching the different accumulated energies for a constant volumetric flow rate of 42 l.min^{-1}. After the phototreatment, samples were filtrated with a 0.45 µm pore size membrane filters and the control parameters were analyzed.

3. RESULTS AND DISCUSSION

It was monitored in the photo degradation process the COD, DOC and the pesticides concentration with HPLC for samples taken at accumulated energies of 0, 18.75, 37.50, 56.25 y 75.00 (kj.L^{-1}). (Figure 2) shows the reduction percentages of COD and DOC for each sample. It was observed that a 57% of degradation was achieved after 5 hours of pretreatment (time required to accumulate 75 kj.L^{-1} of energy with the luminosity conditions for Santiago de Cali). In contrast, it was required 28 days to treat the same wastewater using a biological reactors achieving only a 17.7% of degradation (Barba et al, 2009 (12)). Even though the photodegradation is faster than a common biological treatment, it cannot yet be considered a completely effective process to treat agroindustry effluents contaminated with pesticides.

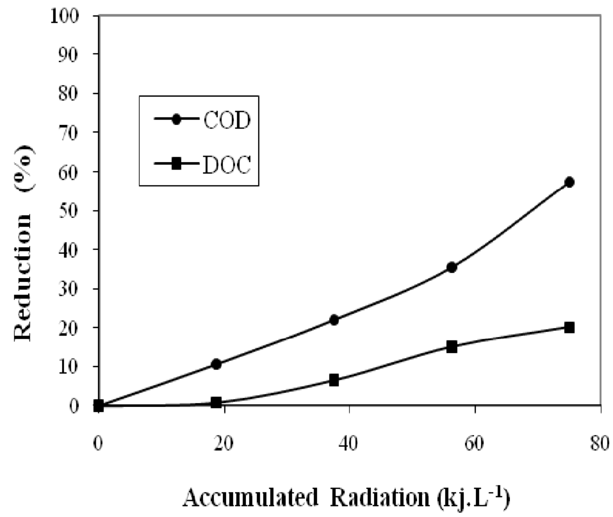


Figure 2. Reduction percentages of COD and DOC of the photo treated samples for each of the assessed accumulated energies.

If the total organic carbon mineralization from the organic matter is considered as a reduction of DOC, it can be concluded that only 23.9% of the pesticides present in the wastewater were mineralized for a maximum accumulated energy of (75 kj.L^{-1}). Nevertheless, this DOC mineralization is low when compared to the results reported by Mondragón et al (2006) (13), who obtained a 57% mineralization in 80 minutes of exposition treating Glyphosate and Terbuthrine in water with a black light lamp, and Hincapié et al (2006) (14), who obtained over 90% mineralization in times shorter than 6 hours for the herbicide Aloclor by photo catalysis with TiO_2 in a parabolic cylindrical collector (PCC).

Due to the low miscibility of the Diuron in water and the TiO_2 that was also suspended, the turbidity in the pesticides samples was high, around 5.9 UNT, and as a result, it restricted the photonic utilization in the reaction, well known as the screening effect and so it decreased the mineralization of the organic matter.

In addition, the reactor employed for the experiments was a flat plate reactor which does not count with a light concentration surface such as the PCC reactor. As a result, the amount of photons received by unit is less with a consequent decrease in efficiency.

As for the COD, it was observed a faster reduction rate than the one for DOC, which indicates the pesticides present in the treated water suffered transformations through oxidation reactions without mineralization. The maximum reduction was 57%, which is lower than the established in the Colombian laws for liquid discharges (Ministerio de Agricultura de Colombia, 1984), so that the treated water cannot be discharged directly to the environment due to a potential risk on the aquatic ecosystems and human health.

The fact that a total COD and DOC degradation was not accomplished does not discard the photo catalysis as an alternative treatment for this kind of wastewater, as the main purpose of this study is to couple photocatalysis to a biological treatment process, so that the phototreated effluent partially decontaminated, is further degraded by the action of microorganisms in the biological reactor.

This way, non-biodegradable agroindustry wastewaters can be treated with photo catalysis to transform the initial components in simpler and less toxic substances suitable for biological treatment.

In that order, Lapertot et al. (2006) identified the ratio COD/DOC as a parameter indicating biodegradability transformation phenomena in wastewater containing toxic substances. The COD decreasing while DOC keeping constant is an indication of the occurrence of transformation processes of the present substances, as the photo catalytic process is degrading the compounds to simpler structures better than mineralizing the organic matter.

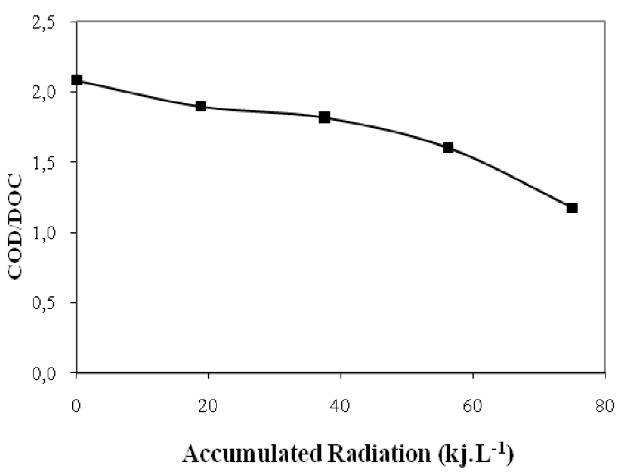


Figure 3. COD and DOC ratio for the photo treated samples taken at accumulated energies of 0, 18.75, 37.50, 56.25 y 75.00 (kj.L^{-1}).

This transformation takes place due to the linkage of bonds in branched chains and aromatic rings, and hydrogen and OH$^{\cdot}$ radicals halides substitution, which generates simpler molecular structure substances and hence biodegradable. The COD/DOC ratio for different accumulated energy levels is shown in Figure 3.

The idea of coupling photo catalytic and biological processes better than having separated process for the treatment of agroindustry effluents contaminated with pesticides is supported by the COD/DOC ratio behavior in the experiments carried out.

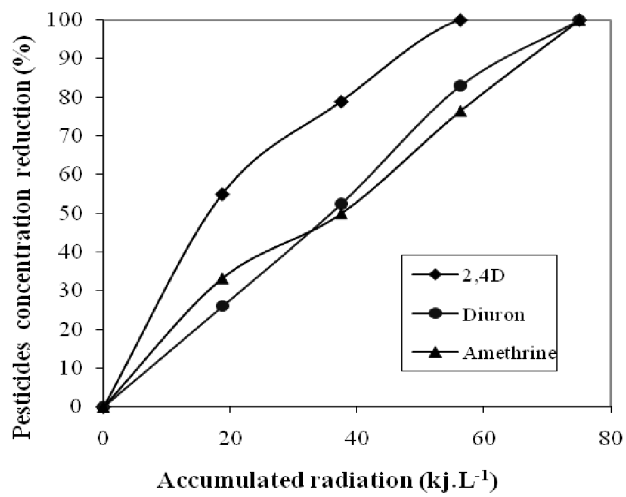
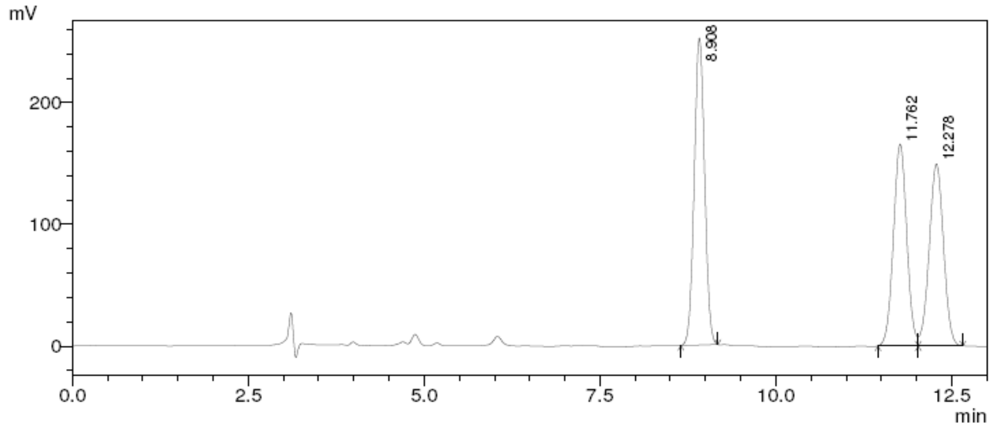


Figure 4. Pesticides concentration reduction percentage followed by HPLC for each of the accumulated energies.

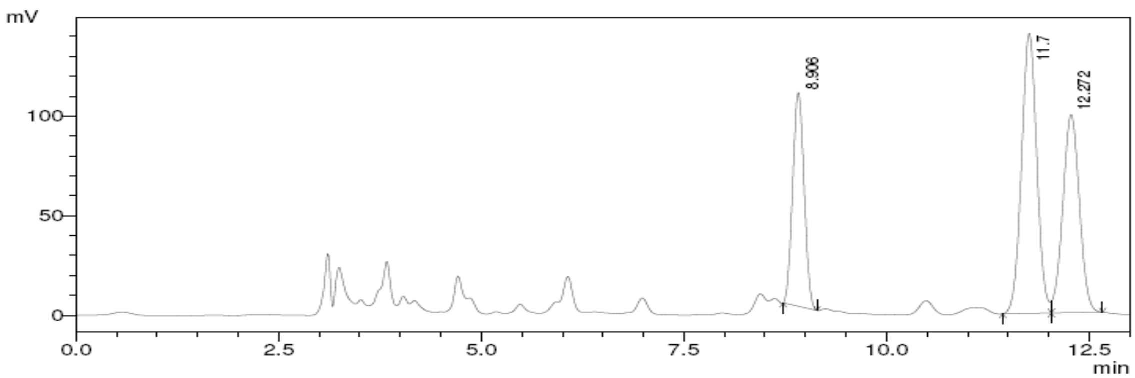
In (Figure 3) is observed that the COD/DOC ratio is inversely proportional to the accumulated energy and decreases with longer exposure times to the solar radiation (2.08 for the simple without photo treatment to 1.18 for the simple exposed to an accumulated energy of 75 kj.L^{-1}). These results indicate that the photocatalysis carries out the transformation of the pesticides of the agroindustry effluents to simpler molecular structure substances, which are supposed to be less toxic and more biodegradable.

One way to verify these partial transformation phenomena on the pesticides is through the concentration of pesticides at different levels of progress of the photo catalysis reaction. Figure 4 shows the reduction percentages of pesticides concentration for each of the

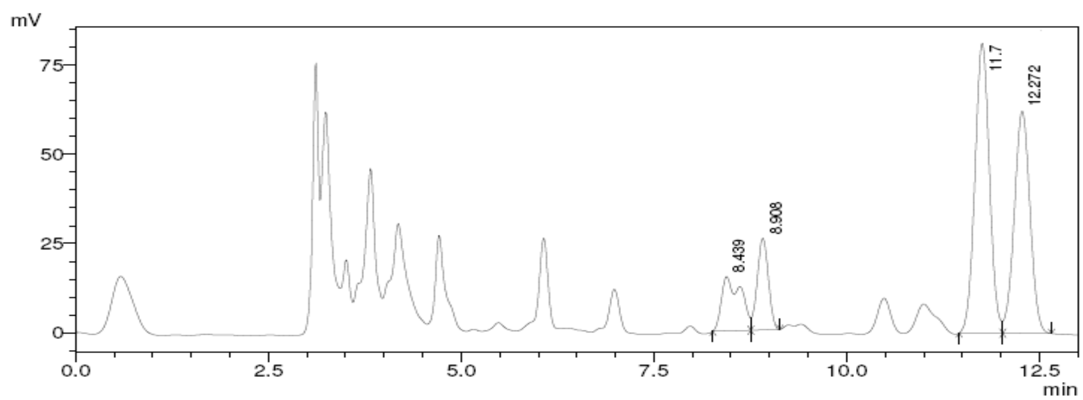
a) 0 kj.L^{-1}



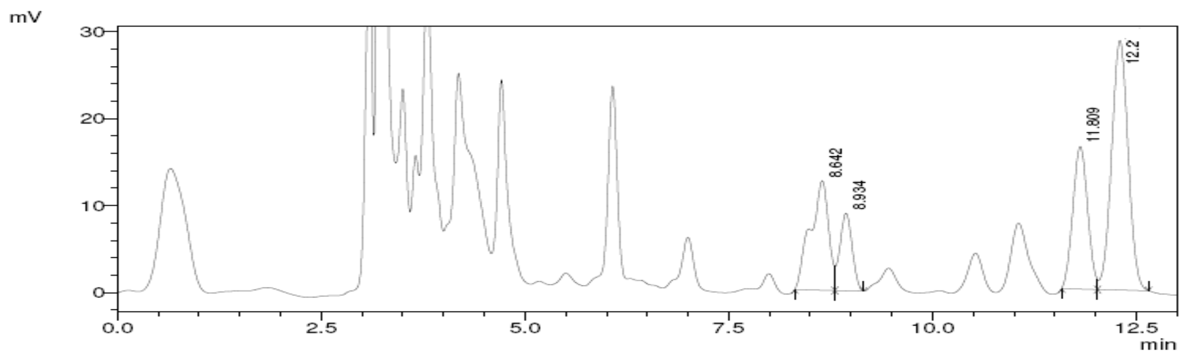
b) 18.75 kj.L^{-1}



c) 37.5 kj.L^{-1}



d) 56.25 kj.L^{-1}



e) 75 kj.L^{-1}

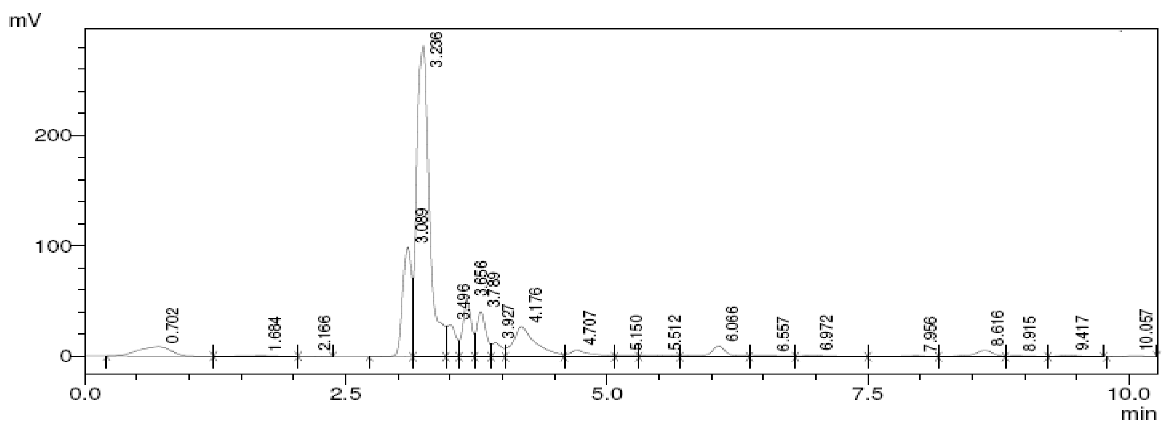


Figure 5. Pesticides analysis by HPLC of the photo treated samples at different accumulated energies

accumulated energies measured with HPLC.

From the pesticides concentration at different accumulated energies is observed that the degradation rates for Amethrine and Diuron are similar, whereas 2,4 D presents the faster degradation rate. In fact, after an accumulated energy of 75 kj.L^{-1} all of the 2,4 D is totally degraded while 17% Diuron and 23.5% Amethrine still remain.

After an accumulated energy of 75 kj.L^{-1}, there are not any of the pesticides in the photo treated effluent, which indicates they were transformed to metabolites and CO_2. This result proves that the photocatalytic reaction acts on the pesticides and transforms the molecules without mineralization, because at the end of the experiments no pesticides could be detected although COD and DOC still remain in the media. Figure 5 shows the HPLC chromatograms of the photo treated samples in the inclined flat plate reactor. It is observed that the pesticides peaks intensity decrease with the reaction progress and new decomposition products (metabolites) appear. In Figure 5a the sample without treatment has three main peaks that correspond from right to left to Amethrine, Diuron y 2,4 D. When the reaction progresses to an accumulated energy of 18.75 kj.L^{-1} these peaks continuously decrease whereas peaks at shorter retention times appear, which indicates the pesticides degradation and metabolites formation in Figure 5b. The same behavior can be observed for accumulated energies of 37.5 kj.L^{-1} (Figure 4c), 56.25 kj.L^{-1} (Figure 5d) y 75 kj.L^{-1} (Figure 5e)

With a higher accumulated energy the metabolites peaks area increase whereas the pesticides decrease and disappear for an accumulated energy of 75 kj.L^{-1}.

The specific compounds that are formed as pesticides degraded products in the photo reactor are unknown. However, as the retention times of these metabolites are short under the analysis conditions, Alltech Econosil C_{18} column and methanol as carrier and phosphate as buffer, it is expected that these correspond to hydrophilic substances, open chain organic compounds or cyclic ones denominated aliphatic hydrocarbons (Lozada, 1998). Aliphatic hydrocarbons biodegradability depends on the type of structure so that open chain hydrocarbons tend to be biodegradable whereas cyclic ones tend to be refractory (Gouch et al., 1992; Colombo., 1996; Hongwei et al., 2004; Del'Arco et al., 2001).

Although the original pesticides are no longer present, the photo treated effluent cannot be discharged to the environment because some substances generated as by-products are even more dangerous , toxic and refractory, that the chemical from which they proceed (Albert, 1999).

Photocatalytic process control

In order to verify that the COD, DOC and pesticides removal obtained in the photo catalytic process are due mainly to heterogeneous photo catalysis and not to photolysis loses caused by radiant energy chemical bonds linkage or any other volatilization or adsorption phenomena on the reactor walls, a blank experiment was carried out without catalysts to obtain COD, DOC and pesticides removal different from that accomplished by photo catalysis. The COD and DOC reduction efficiencies were not higher than 4% so that the observed reduction efficiencies in the photo catalytic process can be attributed to the presence of catalysts and not a photolytic process. At the same time, the pesticides behavior with the photolysis was analyzed and the results showed reduction efficiencies not higher than 5%. This photolysis pesticides removal can be explained with the UV-VIS spectra for 2,4-D and Diuron, where it is observed absorption bands at energetic wavelengths that coincide with those received by sun light, so that the direct irradiation promotes the molecules to excited states that can cause homolysis, heterolysis and photo ionization (Kundu et al., 2005).

Experiments in the darkness with the presence of TiO_2, were also carried out to verify the possible adsorption of pesticides on the catalysts surface, walls and tubes of the photo reactor. This test was conducted during 5 hours, corresponding to the necessary time to reach an accumulated energy of 75kj.L^{-1} (approximated time for a sunny day in Santiago de Cali city). COD, DOC and HPLC pesticides concentration were measured. The results showed reduction percentages of COD and DOC of 2,6% and 2,1% respectively, which indicates that no adsorptive or volatilization phenomena took place, similar to the results obtained for the photolysis.

4. ACKNOWLEDGMENTS

The authors express their gratitude to EPFL and to the Switzerland Cooperation Funds DDC (Direction Du Development et de la Cooperation) for financial support of the Biosolar Detox project (Development of a coupled solar-biological system for the disinfection and elimination of organic contaminants in drinking and wastewaters in rural areas of Colombia) and to the GAOX research group for its cooperation.

5. CONCLUSIONS

. The photolysis degradation rate for agroindustry wastewater treatment is fast in comparison to the degradation rate presented in biological reactors. Through photo catalytic processes COD reduction efficiencies of 57% could be obtained in 5 hours, whereas only 17,7% reduction efficiency was obtained in biological reactors in 28 days.

. The decreasing behavior of the COD/DOC ratio indicates that the toxicity of the agroindustry wastewaters contaminated with pesticides and photo treated with TiO_2 in an inclined flat plate reactor decreases with the progress of the photocatalytic process.

. The photo catalysis for accumulated energies lower than 75 kj.L^{-}1 acts on the pesticides and transform them to less toxic and more biodegradable substances, without mineralization.

. The photo catalysis with TiO_2 in an inclined flat plate reactor can be coupled to biological treatment processes as a viable alternative for the agroindustry wastewater contaminated with pesticides treatment because a high reduction efficiency of contaminants can be obtained (COD and pesticides) in short periods of time.

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